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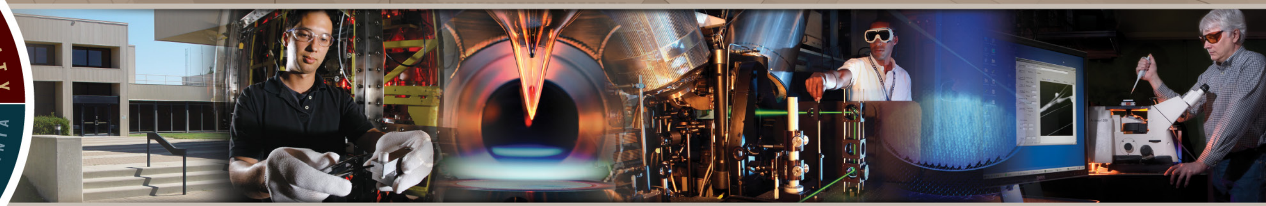

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Picosecond lasers provide researchers with new tools for combustion thermometry

Pure-rotational coherent anti-Stokes Raman spectroscopy (RCARS) provides a useful tool to simultaneously monitor several flame constituents, such as nitrogen and oxygen, and to evaluate each for temperature and relative species concentration. In RCARS, S-branch rotational Raman transitions are excited by the difference frequency between two pump laser photons. Following the excitation of rotational Raman coherences, a narrowband probe beam is scattered from the excited molecules, giving rise to a coherent signal beam that is Raman-shifted to the anti-Stokes side of the probe frequency. The gas-phase temperature can be calculated from the relative intensities of the rotational lines by the use of a frequency-domain CARS model.

In the dual-broadband approach, the pump pulses are both obtained from a single broadband laser. Because the pump photon pairs originate from the same laser, the effect of mode fluctuations is minimized, allowing for more precise temperature determination. Using shorter pulses to drive the RCARS process allows for lower overall energies to be used, which facilitates adaptiation to an imaging configuration.

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Experiments help to develop and validate computer models for low-temperature diesel combustion

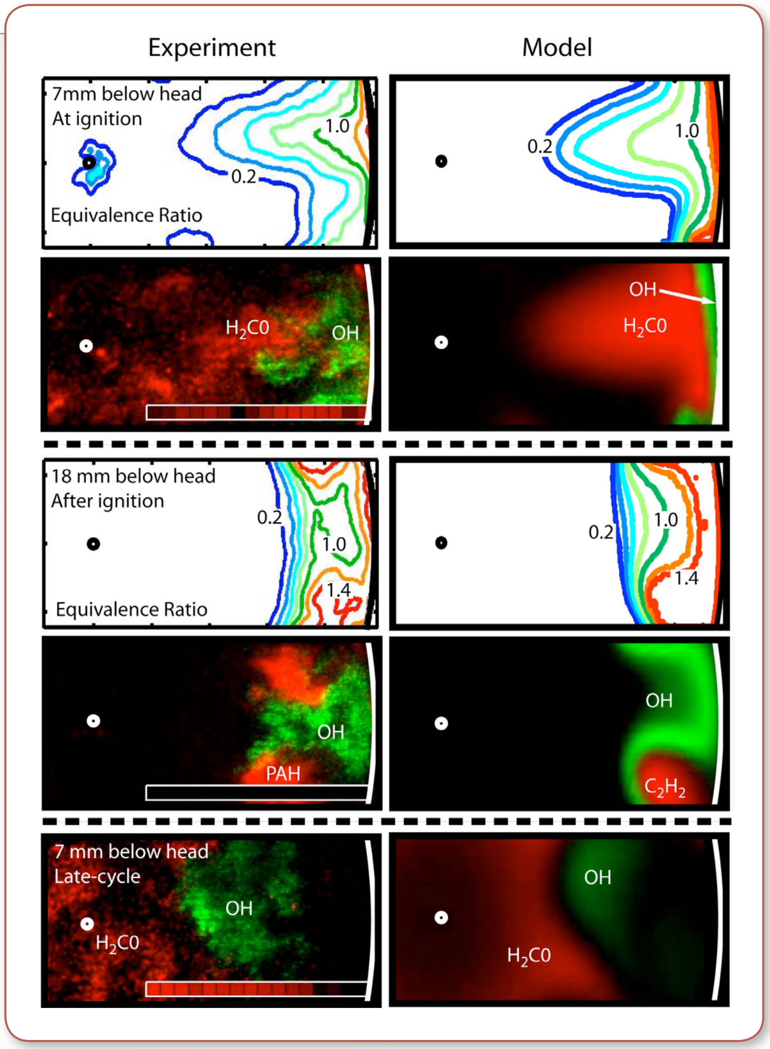

__Figure 1.__ Measured (left) and modeled (right) equivalence ratio (contours) and combustion products (color images) for horizontal planes in a heavy-duty diesel engine combustion chamber. The small dot represents the fuel injector, and the curved line on the right is the piston bowl-wall.

Computer models have become an essential tool for the design and development of diesel engines, but new low-temperature modes of diesel combustion are pushing the envelope of engineering modeling capabilities. Many of the models used for diesel engine simulation were originally developed for conventional diesel combustion and were based on in-cylinder optical diagnostic and other data assembled over the course of decades of research. To extend the model capabilities to modern diesel operational strategies, a new experimental dataset for low-temperature combustion must be built. Furthermore, beyond the development of computer models for engine design, the combination of experimental measurements and validated computer model predictions provides an added opportunity for improved understanding of in-cylinder combustion and pollutant-formation processes.

Recently, CRF researcher Mark Musculus collaborated with Professor Rolf Reitz and Ph.D. student Caroline Genzale (now a CRF post-doc) of the University of Wisconsin

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Newsletter

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Engine Research Center (UWERC) to design experiments to support multi-dimensional model development for low-temperature diesel combustion. The modeling work used an improved version of the Los Alamos KIVA-II computational fluid dynamics code developed at the UWERC. For the experiments, a suite of laser-based optical diagnostics was selected and applied in a heavy-duty optically accessible diesel engine.

The vaporization and mixing of fuel with in-cylinder gases is of paramount importance for the performance of modern engines and it is crucial to accurately model these processes, so the experiments were designed to provide validation data for the model mixing predictions. For direct mixing measurements, the team used planar laser-induced fuel-tracer fluorescence with toluene under non-combusting conditions, a diagnostic previously developed at the CRF heavy-duty diesel engine laboratory (see March/April 2007 *CRF News*). To follow the mixing process through combustion, three other fluorescence diagnostics were selected to indicate extents of fuel–air mixing, based on chemical kinetics considerations for diesel fuels with two-stage ignition.

Fluorescence diagnostics indicate fuel-rich and fuel-lean regions

First, fluorescence of formaldehyde (H_2CO), which is formed during the first stage and consumed in the second stage of ignition, indicates regions that have reached first- but not second-stage ignition. Fuel-lean mixtures reach second-stage ignition relatively late, so persistence of formaldehyde fluorescence late in the cycle indicates likely fuel-lean mixtures as well as regions of incomplete combustion. Second, hydroxyl (OH) radicals, which are formed during second-stage ignition, are most prominent in regions of intermediate stoichiometry between fuel-lean and fuel-rich conditions. As such, fluorescence of OH indicates mixtures with intermediate stoichiometry. Finally, soot precursors, including polycyclic aromatic hydrocarbons (PAH), form after second-stage ignition in fuel-rich mixtures. Broadband PAH fluorescence, verified by their spectral emission signature, therefore indicates both fuel-rich mixtures as well as regions of soot formation.

Figure 1 shows experimental images from the planar laser-induced fluorescence diagnostics (left) and the model predictions of similar quantities (right). In each image, the small dot represents the fuel injector, while the curved line on the right indicates the location of the piston bowl-wall. One of the eight fuel jets, which propagates from left to right, is captured within the field of view of the images. The experimental images also include an indication of the formaldehyde emission signature in the emission spectrum along the jet axis (red-to-black color bar), where red indicates significant formaldehyde fluorescence in the signal.

Captured images validate model predictions

The top two rows of images were captured in a horizontal plane 7 mm below the cylinder head, at ignition. The equivalence-ratio contours show that the model predictions agree well with the experiment, with fuel-lean mixtures (equivalence ratios less than 1) in much of the imaged jet. The measured and modeled formaldehyde (H_2CO) distributions, colored red in the images, persist in the fuel-lean mixtures, while OH (green) appears closer to the piston bowl, where mixtures are of intermediate stoichiometries (equivalence ratios near 1).

The next two rows were acquired shortly after the time of ignition and deeper in the piston bowl (18 mm below the cylinder head). Both the model and experiments predict pockets of fuel-rich mixtures (equivalence ratios greater than 1) at the right of the images. There, at the piston bowl-wall, neighboring fuel jets are deflected into each other, forming fuel-rich pockets between the jets. The fuel-rich regions go on to form soot-precursor species (red), represented by PAH in the experiments and by acetylene (C_2H_2) in the model.

The bottom row of images was acquired late in the cycle, after the majority of combustion was complete, at 7 mm below the cylinder head. Both the experiments and the models show that formaldehyde (H_2CO, red) persists late in the cycle in a broad region in the center of the combustion chamber, while OH (green) is only present on the right side, closer to the piston bowl-wall. The late persistence of formaldehyde in the center of the combustion chamber, along with the absence of OH in the same region, is consistent with fuel-lean mixtures that do not achieve complete combustion and would therefore contribute to pollutant emissions of unburned hydrocarbons.

Beyond simply validating the models, the relatively good agreement between model predictions and the available experimental data is a further opportunity for the models to

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Combustion Research Facility Visitor Program

These visitors will be leaving the Combustion Research Facility at the completion of their tenure.

Ravi Fernandes
8353 post-doc with Craig Taatjes
Ravi carried out fundamental chemistry research in combustion kinetics.

Roland Eisl
8367 visitor with Chris Shaddix
Chris participated in research on oxy-fuel combustion and gasification of coal, and combustion and gasification of biomass lignin.

Curtis Hamman
8351 intern with Alan Kerstein
Curtis, a graduate student and Computational Sciences Graduate Fellow (CSGF) at Stanford, performed his CSGF practicum research with Alan Kerstein. His project involved computational modeling of buoyancy effects seen in fires and other large flames, and also in geophysical and astrophysical flows.

Jean-Guillaume Nerva
8362 visitor with Lyle Pickett
Jean-Guillaume performed research on diesel engine fuel-air mixing, combustion, and emissions processes using various laser-based diagnostics.

Tina Kasper
8353 post-doc with Nils Hansen
Tina investigated the fundamental chemistry of combustion using laser and mass spectrometer diagnostics. She worked primarily at the CRF and also worked at the LBNL Advanced Light Source as part of the Flame Team at the Chemical Dynamics Beamline.

Julien Manin
8362 visitor with Lyle Pickett
Julien performed research on diesel engine fuel-air mixing, combustion, and emissions processes using various laser-based diagnostics.

Venkat Narayanaswamy
8351 visitor with Jonathan Frank
Venkat investigated a new approach to mixture fraction imaging using fluorescence of inert gases.

Thomas Seeger and Johannes Kiefer
8353 visiting researchers with Tom Settersten
Thomas and Johannes collaborated on a joint project: "Development of time-resolved nonlinear Raman spectroscopy." They investigated the use of picosecond laser pulses for time-resolved coherent anti-Stokes Raman spectroscopy in high-pressure environments *(see page 1)*.

Yuxuan Xin
8351 visitor with Jackie Chen
Yuxuan studied direct numerical simulation (DNS) of turbulent syngas jet flames and mechanism reduction strategies.

Chunsang Yoo
8351 post-doc with Jackie Chen
Chunsang made algorithmic advances and developments to Sandia's direct numerical simulation code, S3D. He used the code to investigate the effects of unsteady strain rate on autoignition, extinction, and reignition in a counter-flowing non-premixed hydrocarbon flame.

Advanced Engine Combustion and University HCCI working group meetings held

The Advanced Engine Combustion (AEC) and the University Homogeneous Charge Compression Ignition (HCCI) Engine Combustion working group meetings, organized by Sandia National Laboratories, were held in October at USCAR in Southfield, Michigan. The meetings highlighted the latest progress from all DOE Office of Vehicle Technologies supported research on advanced, low-temperature combustion strategies for high-efficiency, clean engines, and future fuels for these engines. More than 80 representatives from the various AEC Memorandum of Understanding (MOU) industry and national lab partners attended the meetings. (The MOU partners include: GM, Ford, Chrysler, Cummins, Detroit Diesel, Caterpillar, John Deere, General Electric, Chevron, ExxonMobil, ConocoPhillips, BP, SNL, LLNL, LANL, ORNL, and ANL). University attendees from MIT and the Universities of Michigan, Wisconsin, and Illinois joined the group for the University HCCI working group portion of the meetings.

CRF researchers make a splash at international conference

The 3rd International Conference on Hydrogen Safety (ICHS3) was held Sept. 16-18 at the Palais des Congres Ajaccio, Corsica. The ICHS focused on the improvement, knowledge, and understanding of hydrogen safety to foster removal of safety-related barriers to implementation of hydrogen as an energy carrier. The goal of the conference was to improve public awareness and trust in hydrogen technologies by communicating a better understanding of both the risks associated with hydrogen and their management.

CRF staffer Jay Keller moderated a discussion on “hydrogen energy technologies and infrastructure—building a public safety consensus.” Other CRF members presenting papers included Brian Somerday (measurement of fatigue crack growth rates for steels in hydrogen containment components), Bill Houf (ignitability limits for combustion of unintended hydrogen releases), and Bob Schefer (experimental investigation of hydrogen jet fire mitigation by barrier walls). Although the delegation from Sandia was relatively small, they were a major presence, accounting for nearly 11% of the accepted papers.

Sandia has been accepted as a member of the International Association for Hydrogen Safety, and was asked to host the next conference, which will be held in early 2011.

DOE Under Secretary Steve Koonin visits Sandia

Steve Koonin, the Department of Energy’s under secretary for science, visited Sandia California on September 18. He was welcomed by Rick Stulen, vice president of SNL/CA, Chris Moen, deputy VP, and Bob Carling, director of the Transportation Energy Center. The purpose of the visit was to discuss energy strategy and DOE/BES basic research needs in the context of Sandia, industry, and the CRF. Dr. Koonin then toured the CRF facilities and heard presentations by CRF researchers on topics including ultra-cold molecules: basic science underpinning combustion (Dave Chandler), new discoveries in combustion chemistry (Craig Taatjes), high-performance computing for combustion simulation (Joseph Oefelein), high-pressure combustion experiments (Lyle Pickett), and HCCl engine combustion (John Dec).

Dr. Koonin was previously chief scientist for BP, PLC, where he was responsible for guiding the company’s long-range technology strategy, particularly in alternative and renewable energy sources. Koonin joined BP in 2004 following a 29-year career at the California Institute of Technology as a professor of theoretical physics, including a nine-year term as the institute’s provost. He has served on numerous advisory bodies for the National Science Foundation, the Department of Defense and the Department of Energy and its various national laboratories. Koonin’s research interests have included theoretical and computational physics as well as global environmental science. He did his undergraduate work at CalTech and earned his Ph.D from MIT.

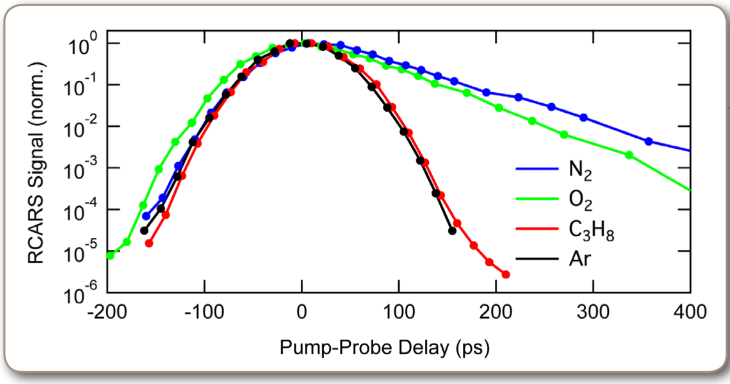

***Figure 1.** Spectrally integrated psRCARS signal as a function of pump-probe delay for various flame species.*

Picosecond lasers (cont.)

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In comparison to vibrational CARS (VCARS), RCARS spectral evaluation is simpler because the large separation of pure-rotational lines reduces the effect of coherent line mixing. The use of picosecond laser pulses provides several advantages to conventional nanosecond CARS setups. As in any nonlinear optical process, signal may arise from non-resonant processes. The coherent non-resonant signal can interfere with the resonant CARS signal, yielding spectra that are more difficult to model and interpret. The non-resonant four-wave mixing signal can be reduced by carefully choosing the polarization combination of the incoming laser beams. However, this method also suppresses the RCARS signal and is susceptible to polarization scrambling caused by scattering or birefringence in the sample.

Using ps pulses and time-delaying the probe pulse provides an alternate method of suppressing non-resonant background, as the lifetime of the non-resonant background is shorter than that of excited rotational Raman coherences. Figure 1 demonstrates this point; the non-resonant signal from Ar is suppressed three orders of magnitude more than the resonant signal from nitrogen and oxygen at a 150-ps probe delay.

CRF researchers Christopher Kliewer, Brian Patterson, and Thomas Settersten, in a collaboration with Thomas Seeger and Johannes Kiefer of the Universität Erlangen-Nürnberg, have investigated the use of time-resolved picosecond RCARS spectroscopy for combustion applications, while CRF researcher Roger Farrow is currently working on a time-domain RCARS fitting model to explicitly account for the J-dependent collisional dephasing with probe delay. In Figure 1, both the nitrogen and oxygen signals persist significantly longer than the argon non-resonant background and the propane signal, which decay much more quickly. The large difference in the signal decay rates allows both nitrogen and oxygen to be effectively used for thermometry even in the presence of large non-resonant or interfering resonant background from the fuel during combustion processes.

Resonant signal may also be a problem during RCARS experiments, especially in a fuel-rich or highly sooting flame, where large hydrocarbon molecules can contribute significantly to the RCARS signal. Because the modeling of the RCARS response of large fuel molecules is highly complex and not well developed, the utility of the technique for fuel-rich flame environments is limited. An additional complication is the generation of resonant smeared vibrational CARS (SVCARS) signal, which arises when the difference frequency between the probe pulse and one of the pump pulses excites a Raman-active vibrational mode of molecules within the interaction volume.

If this occurs, the second broadband pump pulse scatters from the excited ro-vibrational coherence, generating a broad vibrational signal that

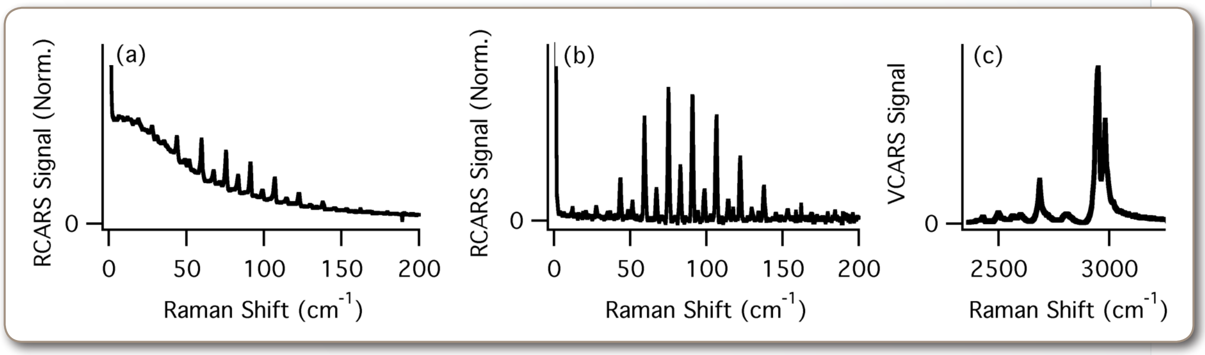

***Figure 2.** PsRCARS spectrum of a 1-bar mixture of 57% propane and 43% nitrogen, using a 633-nm broadband pump and a 532-nm probe with a probe delay of (a) 0 ps and (b) 150 ps. (c) VCARS spectrum of propane using the same 633-nm dye laser as the Stokes pulse and the 532-nm laser as the pump and probe pulses.*

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Computer models for low-temperature diesel combustion (cont.)

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provide cylinder-averaged quantitative predictions not available from planar optical diagnostics. Planar laser diagnostics are limited by the two-dimensional field of the laser sheet, by the available optical access ports, and by diagnostic capabilities for species of interest. The model simulations can help to fill in these holes of missing information. For instance, the simulations predict that emissions of unburned fuel and carbon monoxide, which is difficult to probe with optical diagnostics, arise almost entirely from fuel-lean mixtures throughout a three-dimensional region largely in the center of the combustion chamber.

Finally, the improved and validated models provide a valuable tool for engine designers to explore the effects of geometric and operational variables on in-cylinder combustion and pollutant-formation processes under modern low-temperature combustion modes.

Picosecond lasers (cont.)

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interferes with the RCARS spectra. However, SVCARS signal can be eliminated using time-resolved psRCARS by delaying the probe pulse beyond the envelope of the pump. In this case, there no longer exists a photon pair to drive the vibrational coherence in the SVCARS process.

In Figure 2, panel (a) demonstrates the complicated resonant and nonresonant signal obtained in a fuel/nitrogen mixture—this is the signal one would obtain in a standard nsRCARS experiment. Panel (b) demonstrates that by using picosecond laser pulses and a probe delay, a clean nitrogen spectrum is obtained. Figure 2(c) demonstrates the inadvertent excitation of vibrational coherences using the 532-nm green and 633-nm broadband pulse. To resolve these C-H vibrational modes of the fuel, a second narrowband 532-nm pulse was scattered as a probe. Thus, in Figure 2(a), part of the complicated signal arises from SVCARS, but is eliminated by the 150-ps probe delay shown in Figure 2(b).

The reduced energy required to drive the third-order nonlinear process using ps pulses facilitates adaptation to a 1-D imaging configuration by vertically expanding the three laser beams into sheets as they are horizontally focused to the beam crossing. Some initial results of 1-D imaging of a propane jet nozzle flame are shown in Figure 3. Several advantages have been shown for the use of ps time-resolved RCARS for use in practical combustion related diagnostics. Namely, the suppression of both non-resonant and interfering resonant backgrounds for spectral simplification has been demonstrated, allowing for accurate nitrogen thermometry even in fuel-rich or sooting environments. Further, the reduced energy needed in psRCARS creates less scatter and facilitates imaging applications.

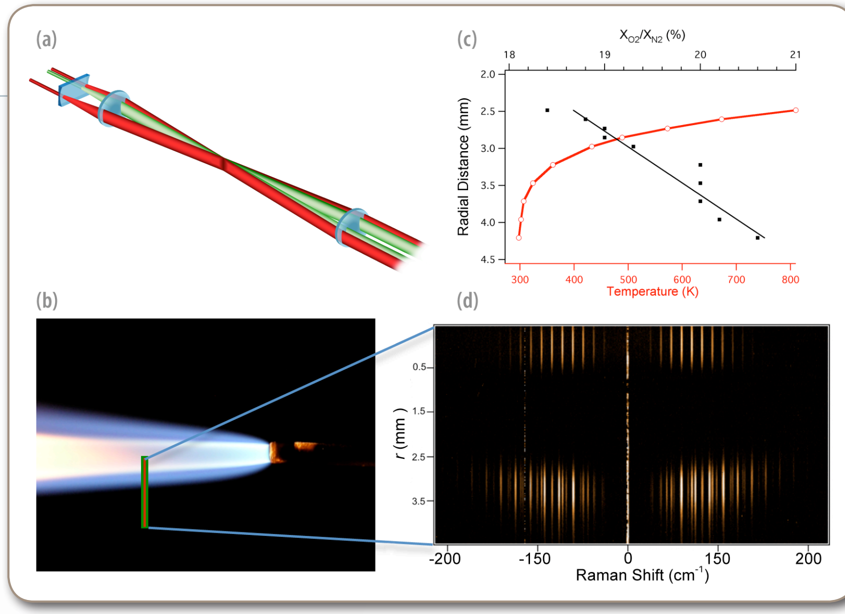

Figure 3. *1-D psRCARS imaging of a propane jet flame from a 1-mm-diameter nozzle using 1.0 slm propane, 1.0 slm oxygen, and 0.4 slm nitrogen, yielding an equivalence ratio of 5.0. (a) Schematic of the imaging configuration surrounding the beam crossing. (b) Photograph of flame emission. (c) Fitted temperatures and oxygen to nitrogen ratios as a function of distance from flame center. (d) Spatially resolved RCARS spectra.*

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